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Differential Quenching of Chromium(III) Photochemistry

Sir:

We report the observation of differential quenching of two reaction modes of a transition-metal complex, $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^+$. The results are interpretable in terms of reaction of two different quartet excited states, and allow some quantitative analysis of the proportion of the two mechanisms and its wavelength dependence.

Wavelength and temperature dependencies of the ratio of reaction modes of mixed-ligand chromium(III) complexes have been reported^{1,2} and have been taken as indicating participation in photosolvation reactions by more than one excited state. Other possible mechanisms have been suggested, however, such as solvent-restricted relaxation³ and/or preferential selection of different solvent environments.⁴

Various approaches have been tried to identify the participating states. Fundamental studies of the emission and absorption properties of the excited states have been important, as has the use of sensitizers and quenchers. Sensitization studies have been somewhat disappointing since the results often parallel the direct photochemistry, exceptions being studies^{5,6} of $[\text{Cr}(\text{NH}_3)_5\text{NCS}]^{2+}$ and $[\text{Cr}(\text{NH}_3)_4\text{Cl}]^{2+}$ where different sensitizers were found to give differing NH_3/X ratios. The apparent lack of spin restrictions on the sensitizer/complex energy transfer has, however, unfortunately blurred the interpretation of such studies.

Quenching experiments have tended to be more definitive.⁷ For a number of complexes exhibiting a single reaction mode, it has been found possible⁸ to quench the phosphorescence more than the photochemistry, showing that at least part of the reaction occurs in competition with intersystem crossing to the thermally equilibrated doublet state. Whether the quenchable reaction occurs directly from the doublet or via back-intersystem crossing is still under active investigation, and it may transpire that both have been demonstrated for particular molecules.⁹⁻¹¹

The extension of such studies to the limited number of molecules which show more than one significant reaction mode offers the hope of gaining additional information from the possible effect of quenching on the reaction mode ratio. An investigation¹¹ of $t\text{-}[\text{Cr}(\text{en})_2(\text{NCS})_2]^+$ revealed that the two reaction modes of this complex were quenched in parallel.

The molecule $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^+$ photoaquates thiocyanate and ethylenediamine (one end) with a wavelength- and tempera-

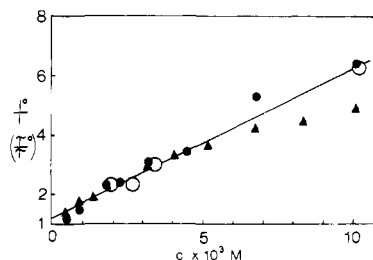


Figure 1. Emission intensity and lifetime quenching. $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^+ = 4.02 \times 10^{-2} \text{ M}$, $1.02 \times 10^{-3} \text{ M HClO}_4$, $[[\text{Cr}(\text{CN})_6]^{3-}] = C \text{ M}$, $t = 5^\circ \text{C}$. Intensity quenching for 546-nm (●) and 436-nm (▲) excitation, corrected for quencher absorbance by Beer's Law. Lifetime quenching for 530-nm (○) excitation. By exclusion of the three high concentration points at 436 nm and giving double weight to the origin, the combined intensity data give a least-squares Stern-Volmer line $I^0/I = 1.03 + 614C$ to which the lifetime data fit well, as shown.

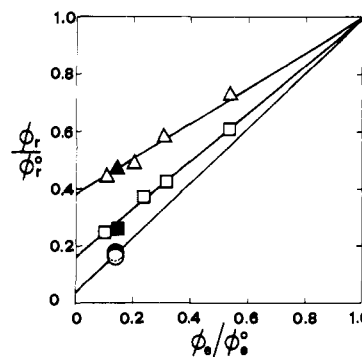


Figure 2. Reaction quenching vs. emission quenching. Thiocyanate mode: $\phi^0 = 0.256$ (546 nm) and 0.268 (436 nm).^{12,21} The quenching results plotted for excitation at 546 nm (●) and 436 nm (○) are each based on three quantum yield determinations with and without quencher, with $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^+ = 4.0 \times 10^{-2} \text{ M}$ in $1.02 \times 10^{-3} \text{ M HClO}_4$, $[\text{Cr}(\text{CN})_6]^{3-} = 1.0 \times 10^{-2} \text{ M}$, $t = 10^\circ \text{C}$. Ethylenediamine mode: $\phi^0 = 0.068$ (546 nm) and 0.105 (436 nm).^{12,21} Points for 546 nm (□) and for 436 nm (▲) are single determinations except for the filled points which are the averages of two determinations. Concentrations as before except for variable $[\text{Cr}(\text{CN})_6]^{3-}$, $t = 5^\circ \text{C}$.

ture-dependent ratio.¹² It also emits¹³ at 717 nm from aqueous solution with quantum yield 10^{-4} at 22°C , and the emission is quenchable by $[\text{Cr}(\text{CN})_6]^{3-}$ and, less efficiently, by $[\text{Cr}(\text{ox})_3]^{3-}$. For excitation at 5°C and 546 nm, where quencher absorption is negligible, the linear Stern-Volmer plot for quenching of the emission intensity is shown in Figure 1. Excitation at 436 nm, where corrections for quencher absorption ranging up to 7% were necessary, yielded data in general agreement although some curvature in the plot is seen. This might be due to uncorrected errors (such nonlinearity could be caused by a few percent of scatter), but certainly for the lower concentrations of quencher excellent agreement was obtained for excitation at the two wavelengths. The least-squares line for the combined data set of Figure 1 yielded a slope of 614 L mol^{-1} (5°C).

The decay lifetime of the emission at 6°C was observed by laser flash techniques¹⁴ to be $1.05 \mu\text{s}$, and the lifetime was quenched by $[\text{Cr}(\text{CN})_6]^{3-}$ with the same Stern-Volmer behavior as the intensity (open points in Figure 1). The excellent agreement between the two sets of measurements shows that the quenching is a collisional process. The lifetime and the Stern-Volmer constant together yield a quenching rate constant of $5.8 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, of the order measured for other systems⁷ involving dynamic quenching between transition-metal complexes. Thus, we have no reason to suspect any anomalies in the quenching by $[\text{Cr}(\text{CN})_6]^{3-}$.

Quantum yields for thiocyanate and ethylenediamine release with and without quencher were measured as before,¹² except for

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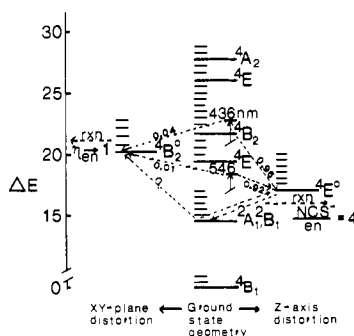


Figure 3. Excited-state levels and possible photoreaction scheme. The vertical axis is to scale as well as the various levels can be estimated from spectral data, calculated splittings,¹⁹ and empiricism.³ Excitation at 546 nm or lower energies populates mainly ${}^4E^0/{}^2A_1$ and 2B_1 , which appear to be in pseudoequilibrium, with a small wavelength- and temperature-dependent population of ${}^4B_2^0$. At 436 nm or higher ligand-field energies, a different and constant ratio of ${}^4B_2^0$ and ${}^4E^0$ is populated. The ${}^4B_2^0$ reaction mode is ethylenediamine loss while ${}^4E^0/{}^2A_1$ and 2B_1 lose ethylenediamine in a 4:1 ratio. The route of these latter two reactions is uncertain. The fractional efficiencies given are suggestive, not definitive.

the use of an Ingold LOT electrode which circumvented the analytical difficulties referred to in the earlier paper. The quantum yields were corrected graphically for thermal reaction of complex and quencher.¹⁵

The results are shown in Figure 2. At 546 and 436 nm and at $[\text{Cr}(\text{CN})_6]^{3-} = 1.0 \times 10^{-2} \text{ M}$, the thiocyanate mode is quenched 83% and 84%, in parallel with the phosphorescence quenching of 85% from Figure 1. In contrast, 71% of the ethylenediamine mode is quenched at 546 nm and only 53% at 436 nm, showing that differential quenching occurs in this system. Extrapolation to infinite quencher concentration yields the values 0.15 and 0.38¹⁵ for the fraction of unquenchable ethylenediamine aquation at 546 and 436 nm, respectively.

Previous quenching studies have revealed a fast photochemistry, competing with intersystem crossing and/or vibrational/solvent-shell relaxation, followed by a quenchable reaction via the doublet state. Detailed studies of $[\text{Cr}(\text{en})_3]^{3+}$ and $t\text{-}[\text{Cr}(\text{en})_2(\text{NCS})_2]^+$ have shown that the phosphorescence yield^{11,17} and the fraction of quenchable reaction¹⁸ both fall for low-energy irradiation wavelengths, owing to lower intersystem crossing yields. For $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^{2+}$, ethylenediamine aquation is the mode which decreases for longer wavelength irradiation, which on the above model implies that this mode arises significantly via the doublet state and should be preferentially quenched, counter to our observations. Such a model involving only 4E and 2E reactivity can be reprieved only by assuming the opposite dependence of intersystem crossing efficiency on energy, an unlikely situation. No simple two-state model appears to explain both our quenching and wavelength dependence results.

A simple solution is to invoke the participation of all three of the states ${}^2(A,B)^0$, ${}^4B_2^0$, and ${}^4E^0$. The possible participation of the two quartet states is suggested by theory¹⁹ and by an analysis

(15) Corrections for quencher photolysis and filtering ($\epsilon_{436} = 7.5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $\phi_{\text{CN}^-} = 0.10$ ¹⁶) seem necessary at 436 nm where the quencher absorbs up to 9% of the absorbed light. The full corrections cause downward curvature in the plot of Figure 2, indicating an overcorrection for photolysis. $[\text{Cr}(\text{CN})_6]^{3-}$ is notoriously difficult to free from the last traces of $[\text{Cr}(\text{CN})_5\text{H}_2\text{O}]^{3+}$, which absorbs strongly at 436 nm and is photoinert. Also, it arises from thermal reaction, particularly in acid solutions. The corrections oppose one another, and we calculate that for the above ϵ value cancellation occurs if $\phi_{\text{effective}} = 0.40$, corresponding to about 60% impurity absorption. These corrections have therefore not been applied. For corrections with $\phi = 0.10$ and 0, respectively, the linear intercepts would be 0.32 and 0.41, giving an idea of the uncertainty.

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of the wavelength and temperature dependencies of the quantum yield ratio for this and other compounds.¹²

Figure 3 shows a possible scheme. Excitation at 436 nm or higher energies leads to vibrationally excited states above a threshold wavelength for energy-independent branching to 4B_2 , 4E , and 2E states, consistent with the short wavelength constancy of quantum yields of reaction.¹² At 546 nm, different proportions of 4B_2 , 4E , and 2E states arise from excitation, and these could be temperature dependent.

The quenchable part of the photochemistry arises from molecules passing through the doublet state; the nature (not amount) of this photochemistry should be independent of excitation wavelength. At 546 nm, and an infinite quencher concentration, 100% of the NCS^- mode and 85% of the ethylenediamine mode are quenched, so that for the doublet-derived photochemistry $\eta_{\text{NCS}^-}/\eta_{\text{en}} = (0.256 \times 1.0)(0.068 \times 0.85) = 4.4$. Similarly, at 436 nm, with 100% quenching of thiocyanate and 62% of ethylenediamine, $\eta_{\text{NCS}^-}/\eta_{\text{en}} = (0.268 \times 1.0)(0.105 \times 0.62) = 4.1$. The good agreement of these two figures provides strong evidence that the same metastable state is being quenched at the two wavelengths.

With the evidence available, it is not possible to decide whether the two reactions occurring via the doublet involve the same or different states. The doublet, the ${}^4E^0$, and even the ${}^4B_2^0$ state, which may well be accessible by reverse intersystem crossing from the doublet, are all possibilities. Theory suggests that the thiocyanate mode might arise from ${}^4E^0$ and the ethylenediamine from ${}^4B_2^0$, both populated by thermal excitation from 2E , but a variety of intermediate situations is also possible. Calculations¹² of the excited-state bond strengths suggest a bond strength difference for the 4E excited state of 31 kJ mol^{-1} for the two modes (NCS^- favored), and for the 4B_2 state of 56 kJ mol^{-1} (en favored), suggesting both modes might occur for ${}^4E^0$, but less probably for ${}^4B_2^0$.

Returning to the absolute yields of the quenchable mode, this analysis yields the values 0.256 and 0.268 for thiocyanate and 0.058 and 0.065 for ethylenediamine at 546 and 436 nm, which parallels other observations of increased intersystem crossing yields for shorter wavelength irradiation and implies further support for our interpretation of the results.

It has recently been proposed that the doublet state reacts directly^{9,10} and furthermore that the doublet reaction mode corresponds to the dominant ground-state reaction.²⁰ Our findings are in conflict with the latter proposal unless one assumes that the predominant thiocyanate mode arises from ${}^4E^0$ and the quenchable ethylenediamine (the dominant ground-state thermal reaction) from doublet.

The unquenchable reaction shows absolute yields for ethylenediamine loss of 0.010 at 546 nm and 0.040 at 436 nm. Nothing definitive can really be said about the states leading to this reaction. It could be prompt, but why then would it be so specific? The molecular orbital theory suggests it more probably occurs during or after relaxation to the 4B_2 state. If so, the above values correspond to the product of the efficiency of 4B_2 reaction and the internal conversion quantum yields to 4B_2 . Although the product cannot be decomposed, the reaction efficiency of 4B_2 has to be fairly close to unity, or a large quantum yield reduction for emission and quenchable reaction on irradiation to shorter wavelengths would be expected.

In summary, the differential reaction quenching of $t\text{-}[\text{Cr}(\text{en})_2\text{NCSF}]^+$ points to participation of two quartet states in addition to the doublet. Reaction via the quenchable route yields $\phi_{\text{NCS}^-}/\phi_{\text{en}} \approx 4$ while the unquenchable route yields only ethylenediamine. Both modes increase in absolute yield on irradiation to shorter wavelength, but the proportional increase in the unquenchable mode is the larger. The proportion of the unquenchable reaction is not only wavelength dependent but, from our earlier data,¹² also probably temperature dependent. The results show that, for these compounds, not only the lowest excited

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state of a given multiplicity may react.

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Optical Resolution of the D- and L-Amino Acid Family by Liquid-Solid Chromatography

Sir:

Recently, we have reported the development of a technique with a chiral amide-bonded stationary phase [(*N*-acyl-L-valyl-amino)propyl silica gel] in liquid chromatography, which by recognition of molecular chiralities permits separation of difficult mixtures of enantiomers.¹⁻³ This technique depends entirely on hydrogen-bond association, and involves no strong complexations such as host-guest,^{4,5} metal-chelate,⁶⁻⁹ and charge-transfer complexations.^{10,11} Our results seem to be of interest since hydrogen bonding is frequently involved in enzymatic chiral recognition in spite of its facile and flexible interaction, and most importantly, its weak association energy. The effect of changing *N*-acyl groups on the stationary phase has been tested to obtain the maximum resolution offered by (*N*-formyl-L-valylamino)propyl (FVA) silica gel.³ We report in this paper that through effective derivatization of solutes the scope of this method can be extended to almost all derivatives in the amino acid family.

Evaluation of derivatizations for improving the resolution was accomplished by systematic *N*-acylations and *O*-alkylations of leucine, which was selected as a typical solute as shown in Table I. The separation factors, i.e., enantioselectivity, depended upon changes involving the *O*-alkyl group while the separation factors were not influenced by *N*-acyl substituents. Increasing the bulkiness of *O*-alkyl moieties afforded larger separation factors, with the most effective value being obtained for the *O*-*tert*-butyl ester.

Thus, we applied the *N*-acetylation-*O*-*tert*-butylation procedure to other enantiomers of the amino acid family illustrated in Table II. Binary solvent systems in chromatography were optimized by using stronger components such as diethyl ether, methylene chloride, and chloroform in place of 2-propanol. The nonpolar diluent was *n*-hexane, and solvent mixtures containing 2-propanol were kept at 40 °C, with all others at 20 °C. The most effective separation factors were obtained for separations 1-11 with diethyl ether, for separations 12 and 13 with methylene chloride, and for separations 14 and 15 with chloroform. In each case, other binary solvent systems, such as 2-propanol-*n*-hexane, were tried and found

Table I. Resolution of D- and L-Leucine Derivatives (CH₃)₂CHCH₂CH(COOR¹)NHCOR² with a FVA Column^a

derivative		mobile phase, % (v/v) of 2-PrOH in <i>n</i> -hexane	capacity factor ^b <i>k'</i>		separation factor, ^c <i>a</i>
R ¹	R ²		D	L	
Me	H	6	3.25		1.00
Me	Me	6	3.35	3.66	1.09
Me	Et	4	2.36	2.63	1.11
Me	<i>i</i> -Pr	2	3.00	3.39	1.13
Me	<i>t</i> -Bu	0.5	2.65	2.93	1.11
Me	Me	4	5.50	6.05	1.10
Et	Me	3	4.98	5.74	1.15
<i>i</i> -Pr	Me	2.5	4.71	5.65	1.20
<i>t</i> -Bu	Me	4	2.03	2.54	1.25
<i>t</i> -Bu	Me	2	4.84	6.70	1.38

^a The column was 20 × 0.4 (i.d.) cm stainless-steel tubing and was packed by a high-pressure slurry technique.³ It contained approximately 2 g of FVA silica gel and possessed a dead volume of 1.70 mL with it attached to the liquid chromatograph. The chromatographic runs were made at a constant flow rate of 1 mL/min for doubled FVA columns. The column temperature was 40 °C. In all runs, about 40 μg of racemic leucine derivatives, dissolved in 4 μL of chloroform, was injected onto the column during flow. The appearance of enantiomers in the column eluate was detected by ultraviolet absorption at 230 nm. ^b *k'* = (retention time of enantiomer - dead time)/dead time. ^c *a* = *k'* of L enantiomer/*k'* of D enantiomer.

Table II. Resolution of Enantiomers of *N*-Acetyl Amino Acid *tert*-Butyl Esters^a

separation	amino acid	strong solvent in <i>n</i> -hexane (%, v/v)	<i>k'</i>		<i>a</i>	resolution, ^b <i>R_s</i>
			D	L		
1	Leu	Et ₂ O (80)	3.12	4.33	1.39	4.21
2	Val	Et ₂ O (80)	3.41	4.69	1.38	4.17
3	Nle	Et ₂ O (80)	3.13	4.28	1.37	3.99
4	Nva	Et ₂ O (80)	3.63	4.89	1.35	3.88
5	Abu	Et ₂ O (80)	4.12	5.37	1.30	3.39
6	Ala	Et ₂ O (80)	4.83	5.95	1.23	2.66
7	Ile	Et ₂ O (80)	3.16	4.32	1.37	4.00
8	<i>O</i> - <i>t</i> -BuSer	Et ₂ O (80)	2.13	2.82	1.32	3.12
9	<i>O</i> -AcTyr	Et ₂ O (80)	7.67	9.33	1.22	2.70
10	<i>O</i> - <i>t</i> -BuAsp	Et ₂ O (80)	2.57	3.10	1.21	2.13
11	<i>O</i> - <i>t</i> -BuGlu	Et ₂ O (80)	3.57	4.33	1.21	2.30
12	<i>S</i> -BzlCys	CH ₂ Cl ₂ (30)	1.77	2.31	1.31	2.85
13	<i>N</i> - <i>t</i> -BuTrp	CH ₂ Cl ₂ (30)	1.88	2.58	1.37	3.50
14	PheGly	CHCl ₃ (30)	2.28	3.02	1.32	3.18
15	Phe	CHCl ₃ (30)	1.96	2.71	1.38	3.64
16	<i>N</i> -AcLys	2-PrOH (12)	6.83	7.17	1.05	0.60
17	Gln	2-PrOH (8)	17.63 ^c		>1.00	<0.30
18	Pro	2-PrOH (4)	2.77		1.00	

^a The column temperature was 20 °C for separation 1-15, and detection for separations 12-15 was done at 254 nm with all others at 230 nm. Columns and other operating details are as described in Table I legend. ^b *R_s* = $1/4(a-1)N^{1/2}[k/(1+k)]$, where *k* = (*k'* of D enantiomer + *k'* of L enantiomer)/2 and *N* = 16(retention time of enantiomer/bandwidth of peak)². ^c Shoulder was definitely detected.

to have smaller separation factors; however, peak separations were still definite in all cases. Some of the results are illustrated in Figure 1.

Systems using 2-propanol-*n*-hexane had separation factors in the range of 1.05-1.21 and exhibited weak but sufficient chiral recognition. These values increased dramatically to a maximum of 1.39 when the stronger solvent component was changed from 2-propanol to diethyl ether, methylene chloride, or chloroform. These results suggest that the hydrogen bonding between stationary surface and solute is the determining factor for the enantioselection in aprotic solvents rather than in protic solvents.

The retention of L isomers was always larger than that of D isomers, showing the hydrogen-bond associations between the

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